

# First-principles investigation of uranium monochalcogenides

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We present first-principles investigation of the electronic structure and magnetic properties of uranium monochalcogenides: US, USe, UTe. The calculations were performed by using recently developed LDA+U+SO method in which both Coulomb and spin-orbit interactions have been taken into account in rotationally invariant form. We discuss the problem of choice of the Coulomb interaction value. The calculated [111] easy axes agree with those experimentally observed. The electronic configuration  $5f^3$  was found for all uranium compounds under investigation.

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Local Spin Density Approximation (LSDA) [1] based on the density functional theory is a widely used method for electronic and magnetic structure investigations of modern materials. Despite the success in description of wide band materials, LSDA fails when applied to describe transition metal or rare earth metal compounds. For example, it gives a metallic ground state in case of  $3d$  insulators (such as CuO, CoO, FeO) or underestimates an energy gap and local magnetic moments values for NiO [2]. Another important drawback of LSDA is an underestimation of the orbital moment value  $\mathbf{L}$ . LSDA calculations with the spin-orbit (SO) coupling taken into account yield the orbital moment value about two times smaller than its experimentally observed counterpart [3, 4]. While  $\mathbf{L}$  is small for transition metal compounds and one can neglect it, this is not the case for  $4f$ - and  $5f$ -metal systems where the value of the orbital moment is larger than the spin one.

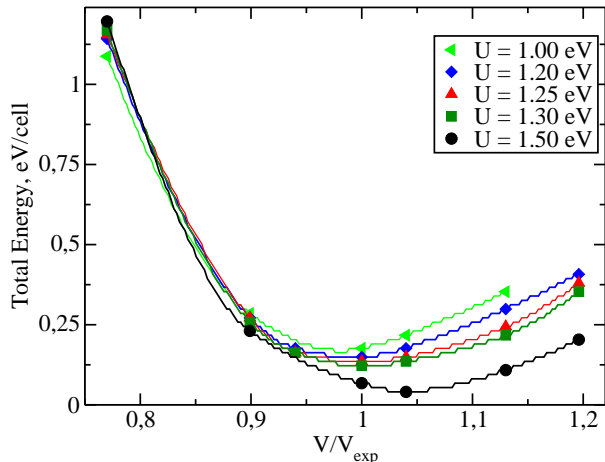
The problem of the underestimation of  $\mathbf{L}$  comes from the orbital independent nature of the LSDA potential and can be solved by using LDA+U+SO approach, where spin and orbital dependent on-site potential is provided [10]. It results in orbital polarization increasing and, hence, it increases the value of the orbital moment and the magnetic anisotropy energy [11]. The results of previous theoretical [15] and experimental [7] studies demonstrate that the orbital polarization mechanism plays a crucial role in  $5f$  actinide systems, such as US, UTe and USe.

In this paper we report the results of first-principle LDA+U+SO investigations of uranium monochalcogenides: US, USe and UTe. Choice of the screened Coulomb interaction is discussed and the obtained results are compared with the LDA+SO and experimentally observed one.

The investigated uranium monochalcogenides have the NaCl-type crystal structure and are ferromagnets with Curie temperature 178 K, 160 K and 102 K for US, USe, UTe respectively [5]. Despite of simple and high symmetric crystal structure ( $Fm\bar{3}m$ ), the easy axes are arranged along the diagonal of the cubic cell [111] [6, 7, 8]. In our calculations we use the tight-binding linear muffin-tin orbital approach in atomic sphere approximation (Stuttgart LMTO47 code) [12] with conventional local-density approximation and take into account the on-site Coulomb and spin-orbit interactions (LDA+U+SO) [10]. The LMTO basis set contains the following states: U( $7s, 6p, 6d$ ), S( $3s, 3p, 3d$ ), Se( $4s, 4p, 4d$ ) and Te( $5s, 5p, 5d, 5f$ ). The Brillouin zone integration has been performed on the  $8 \times 8 \times 8$  grid.

The value of screened Coulomb interaction,  $U$ , and Hund's exchange,  $J_H$ , are cornerstones of the LDA+U+SO method. While determination of former is a complicated issue and depends strongly from screening in solids, the later is hardly changed from its atomic (ionic) value. The constrain LDA method described in Ref. [14] gives the value  $J_H = 0.48$  eV for all compounds and it is in good agreement with estimated in Ref. [10]. This value of Hund's exchange will be used through the paper.

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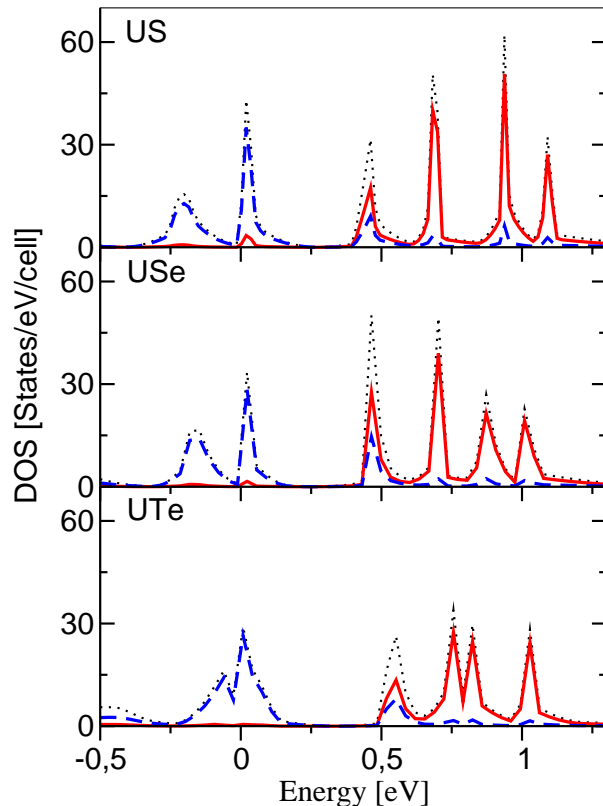


Total energy vs. cell volume for different  $U$  values obtained in LDA+ $U$ +SO calculations for US.

It is well-known that the  $U$  value depends strongly from number of screening channels taken into account. For a free ion the Coulomb parameter,  $U$ , is about 20 eV, while its value in the solid varies from 4 eV to 10 eV for 3d-metals. In actinides, the value of the on-site Coulomb interaction becomes smaller since 5f states are more expanded in real space than 3d one. Several features that can be calculated using band structure methods, e.g. magnitude of local magnetic moment, density of states at the Fermi energy for metals or energy gap for insulator depends strongly on the Coulomb parameter. Therefore, the first important task of investigation is to define  $U$  in reliable way. In this paper we demonstrate different approaches to calculate the value of screened Coulomb repulsion.

One way is to adapt the Coulomb interaction value to have certain calculated and experimentally measured physical quantities coinciding. For example, T. Shishidou *et al.* [15] have shown using a Hartree-Fock approximation with  $U$  as a free parameter that calculated and experimental values of the local magnetic moments and the direction of the easy axes agree well for  $U=0.76$  eV. In this work we fit an equilibrium volume of US by varying  $U$ -parameter. The result is shown on the Fig. 1. The calculated equilibrium volume is close to the experimental one at the value of  $U=1.25$  eV and it will be used for the uranium compounds under investigation.

Another way to calculate the value of screened Coulomb interaction from first principles is the supercell procedure [14] that takes into account  $s$ -,  $p$ - and  $d$ -screening channels. In the framework of this procedure, the calculated Coulomb repulsion is equal to 3.6 eV for US. This value is larger than reported by Shishi-

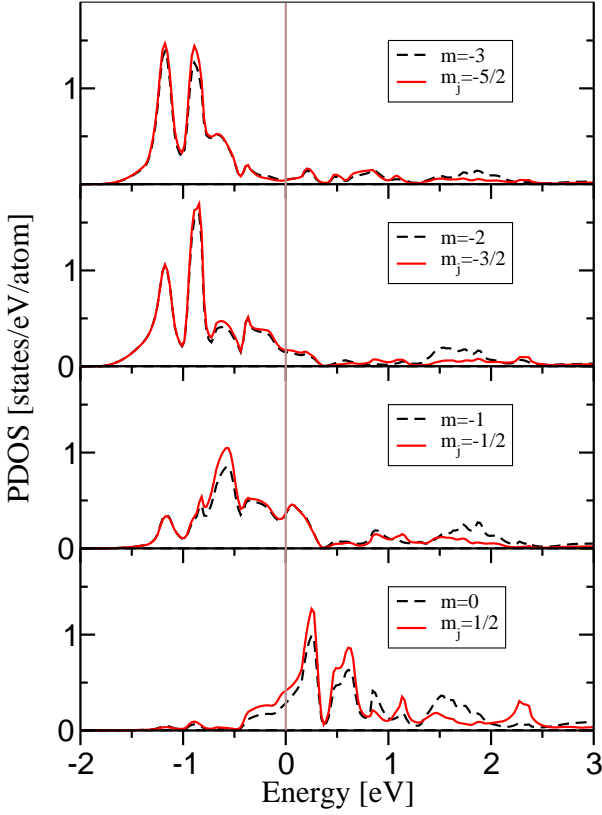


LDA+SO partial DOS for uranium monochalcogenides.  $j=5/2$  is represented by dashed blue line,  $j=7/2$  is represented by solid red line and its sum is a dotted black curve.

dou [15] and have found in this work. To understand this discrepancy we will analyze the LDA+SO densities of states presented in Fig. 2. One can clearly see that  $j=5/2$  and  $j=7/2$  subbands are well separated due to a strong spin-orbit interaction (the value of spin-orbit coupling  $\lambda=??$  eV) and, hence, for the investigated uranium monochalcogenides one more screening channel should be taken into account. The additional screening channel of conducting  $j=7/2$  states leads to much smaller  $U$  values which are 0.82 eV, 0.98 eV and 0.75 eV for US, USe and UTe, respectively. These values are closer to one used in Ref. [15].

We have performed two series of calculation *i)* with the value of Coulomb interaction obtained by fit of equilibrium volume,  $U=1.25$  eV, for all three compounds and *ii)* with three different  $U$  values calculated in supercell procedure which takes into account 7/2-5/2 screening.

We emphasize here that in all our calculations we have started with initial directions of spin and orbital moments coincided with the crystallographic  $c$ -axes.



LDA+U+SO partial DOS for US. Four most occupied orbitals shown only. Density of states in Russell-Saunders ( $LS$ ) representation is shown by dashed black line. Red solid line shows PDOS in  $jj$  coupling scheme.

The resulting self-consistent  $\mathbf{S}$  and  $\mathbf{L}$  vectors were found to be anti-parallel to each other and aligned along  $[111]$  direction. It coincides with easy axes experimentally observed for all compounds [6, 7, 8].

In order to analyze different contributions of the  $5f$  states to the resulting densities of states we have chosen a new local coordinate system with  $z$ -axis directed along total moment  $\mathbf{J}$ . The partial density of states for 4 orbitals with maximal occupation numbers in both  $jj$ - and  $LS$ -representations are shown in the Fig. 3. Based on the obtained densities of states we can conclude that there are three occupied orbitals and one partially occupied orbital which forms the peak on the Fermi level. The similarity of PDOS shape in both  $jj$ - and  $LS$ -schemes confirms the applicability of intermediate coupling scheme. Another argument to confirm the intermediate character of coupling is an occupation matrix which has a large off-diagonal elements in either  $jj$  or  $LS$  coupling schemes. The magnitude of the largest off-diagonal element in both schemes is just ?? per cents smaller than diagonal one. This result can be explained

|     | $J$  | $\mu_{jj}^{calc}$ | $\mu_{LS}^{calc}$ | $\mu_{eff}$ [16] | $\mu_{neut}$ [17] |
|-----|------|-------------------|-------------------|------------------|-------------------|
| US  | 3.18 | 3.14              | 2.66              | 2.2              | $1.7 \pm 0.03$    |
| USe | 3.38 | 3.31              | 2.81              | 2.5              | $2.0 \pm 0.1$     |
| UTe | 3.51 | 3.42              | 2.91              | 2.8              | $2.2 \pm 0.1$     |

Comparison of LDA+U+SO calculation results obtained for  $U=1.25$  eV and experimental data ( $g_{LS}=0.73$ ,  $g_{jj}=0.86$ ).

|     | $J$  | $\mu_{jj}^{calc}$ | $\mu_{LS}^{calc}$ | $\mu_{eff}$ [16] | $\mu_{neut}$ [17] |
|-----|------|-------------------|-------------------|------------------|-------------------|
| US  | 2.78 | 2.79              | 2.37              | 2.2              | $1.7 \pm 0.03$    |
| USe | 3.18 | 3.14              | 2.66              | 2.5              | $2.0 \pm 0.1$     |
| UTe | 3.30 | 3.24              | 2.75              | 2.8              | $2.2 \pm 0.1$     |

Comparison of LDA+U+SO calculation results (Coulomb interaction values are 0.82 eV, 0.98 eV and 0.75 eV for US, USe and UTe, respectively) and experimental data ( $g_{LS}=0.73$ ,  $g_{jj}=0.86$ ).

as a strong competition of a strong spin-orbit interaction and intra-atomic exchange interaction. Indeed, the values of spin-orbit coupling,  $\lambda=??$  eV, is comparable with the Hund's exchange,  $J_H=0.48$  eV. Therefore, in the situation where the Hund's exchange, voting for the Russell-Saunders representation, cannot beat the spin-orbit interaction, favoring  $jj$  representation, the intermediate coupling scheme is more desirable for all compounds under consideration.

Experimentally observed values of the  $5f$  magnetic moments are much smaller than expected for a free ion with  $f^3$  configuration (see Table 2). We have calculated the effective magnetic moments for US, USe, UTe using the following expression:  $\mu_{eff}^2 = g\mu_B J(J+1)$  where Landé factors for  $f^3$  configuration are  $g_{LS}=0.73$  and  $g_{jj}=0.86$  for  $LS$  and  $jj$ -couplings, respectively. The comparison of the calculated and experimental magnetic moments is presented in Tables 2 and 3. Theoretical moments seem to be overestimated but howbeit agree reasonably well with the experimental data. This overestimation is a result of the large on-site Coulomb interaction,  $U=1.25$  eV. The results of second series of LDA+U+SO calculation with  $U=0.82$  eV, 0.98 eV and 0.75 eV for US, USe and UTe, respectively, are presented in Table 3. One can clearly see that there is a good agreement between theoretical and experimental values.

To conclude, we have performed first-principles investigations of uranium monochalcogenides: US, USe and UTe. The choice of Coulomb parameter  $U$  has been discussed. We have demonstrated that supercell procedure with additional screening channels produces the

value of screened Coulomb interaction which gives the values of effective magnetic moments in better agreement with the experimental data. It can be traced to the fact that this is an electronic degrees of freedom based method while fitting of  $U$  to have the calculated and experimental volumes coinciding should better describe phonon properties of solids. We have analyzed LDA+U+SO results in two different coupling basis of  $LS$  and  $jj$  types. It was found that for the studied uranium compounds the intermediate coupling scheme is more preferable. Based on the obtained occupation matrices and partial densities of states we have concluded about  $5f^3$  electronic configuration for the uranium compounds.

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